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Improvement of mechanical properties for PP/PS blends by in situ compatibilization

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Abstract

The effect of the in situ compatibilization on the mechanical properties of PP/PS blends was investigated. The application of Friedel–Crafts alkylation reaction to the PP/PS-blend compatibilization was assessed. Styrene/$AlCl_3$ was used as catalyst system. The graft copolymer (PP-*g*-PS) formed at the interphase showed relatively high emulsifying strength. Scission reactions, occurring in parallel with grafting, were verified for PP and PS at high catalyst concentration, but no crosslinking reactions were detected. Tensile tests were performed on dog-bone specimens of the blends. Both elongation at break and toughness increased with catalyst concentration. At 0.7% $AlCl_3$, a maximum was reached, which amounted to five times the value of the property for the uncompatibilized blend. At higher catalyst concentrations these properties decreased along with the PP molecular weight due to chain-scission reactions. On the other hand, the tensile strength did not change with the catalyst concentration. The in situ compatibilized blends showed considerable improvement in mechanical properties, but were adversely affected by chain scissions at high catalyst contents.

Keywords: PP/PS blends; In situ compatibilization; Mechanical properties

1. Introduction

The engineering applications of commodity thermoplastic blends have continuously grown up during the last few years, and are mainly focused on the development of tailor-made and novel material properties. Positive features for their success include good cost-performance balance, wide range of processing-transformation possibilities, and recycling simplicity [1–3]. It is well known that the direct blending of two or more thermoplastic polymers in appreciable proportions causes phase segregation, low interfacial adhesion and poor mechanical properties [2–6]. The adhesion between these polymers is low because very few molecular chains connect the phases by traversing the interphase. However, an adequate compatibilization process increases the phase adhesion, reduces the interfacial tension and stabilizes the morphology by inhibiting droplet coalescence [6–8]. Consequently, the mechanical properties can be improved.

Within the phase compatibilization methods, reactive processes have proved to be the best ones [2,3]. The compatibilizer, usually a copolymer, is generated in situ by a reaction between the homopolymers. In particular, the low-cost Friedel–Crafts (FC) alkylation reaction is an attractive route to compatibilize thermoplastic blends that contain PS. By this reaction, a hydrocarbon chain can be chemically bonded to the PS benzene ring through an aromatic electrophilic substitution. The resulting graft copolymer (polyolefin-*g*-PS), which is located at the interphase, will behave as an in situ compatibilizer for the specific polyolefin/PS blend [9–11]. These compatibilization procedures require a fine control of the copolymer concentration. It is well known that the in situ compatibilization effect becomes more significant as the interfacial agent concentration approaches saturation. At this point the critical micelle concentration condition (cmc) is reached [3,8].

In our previous work [10], the application of the FC reaction to the compatibilization of PP/PS blends was studied. The emulsifying strength of the graft copolymers formed was assessed and the cmc condition was determined.

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The amount of grafted PS, as well as the possible side reactions, namely PP and PS chain scission and cross-linking, were worked out. It was determined that for high catalyst concentrations, the chain scission is evident in both base polymers (PP and PS). All reaction products were characterized by careful selective solvent extraction separation, followed by a combination of SEC and FTIR techniques.

In the present work, mechanical properties of in situ compatibilization PP/PS blends were assessed. The compatibilization was performed by means of the FC reaction. The amount of copolymer formed and the degree of scission produced, which are determined by the catalyst concentration used in this reaction, were related to the morphological characteristics and mechanical properties of the blends.

2. Experimental

2.1. Materials

Polystyrene Lustrex HH-103 (PS) supplied by UNISTAR, and polypropylene Cuyolen 1102 (PP) from Petroquímica Cuyo SA, were used as basic materials. The alkylation reaction was catalyzed by a system containing Merk anhydrous aluminum chloride ($AlCl_3$), (>98% purity), and styrene (>99% purity)[1].

2.2. Blending

2.2.1. Physical blend (PB)

PP (80%)/PS (20%) blends were prepared. Blending was carried out under nitrogen atmosphere, in a batch mixer (Brabender Plastograph W50) at 200 °C. The mixing procedure includes the initial melting of PS, and subsequent incorporation of PP. Mixing was performed at 60 rpm for 24 min.

2.2.2. Homopolymers (PP and PS)

The blending routine was carried out on the pure homopolymers to check possible degradation due to processing. PP and PS were melted at 200 °C, in a batch mixer under nitrogen atmosphere at 60 rpm during 24 min. Samples, called PPp and PSp, were collected and characterized.

2.2.3. Reactive blends (RB)

The reaction was performed in the same batch mixer and at the same conditions as used for physical blends. The catalyst was added to the already melted and mixed homopolymers. A set of RB was prepared using 0.3% styrene and different concentrations of $AlCl_3$.

2.2.4. Reacted homopolymers

Pure PP and PS were reacted at the same conditions as used for RB. The reacted PP and PS were named RPP and RPS, respectively. Table 1 summarizes the description of all the samples prepared.

2.3. Characterization

2.3.1. Size exclusion chromatography

SEC chromatograms of PP, PS, PPp, PSp, RPP, RPS, were obtained in a Waters Scientific Chromatograph model 150-CV. The different samples were dissolved in 1,2,4-trichlorobenzene (0.0125% BHT) at the same initial concentration and then, injected at 135 °C. Molecular weight distributions were also calculated for PP, PS, PPp, PSp, RPP, RPS. Results are shown in Tables 2 and 3.

2.3.2. Mechanical properties

Tensile tests were carried out on an Instron tester with crosshead speed of 5 mm/min at room temperature. Dog-bone tensile specimens were cut from plates prepared by compression molding. The bone specimen dimensions were scaled to one third of ASTM D638M norm dimensions (specimen type IV). Tensile strength, elongation at break and energy at break were determined from tension–deformation curves for all samples.

2.3.3. Fourier transform infrared spectroscopy

This technique was used to analyze the possible oxidative degradation of the materials. The typical carbonyl oxidative absorption peak, at about 1700 cm^{-1}, was looked for in all of the samples. The general shape of the spectra from PPp, PSp was compared with those from the starting materials PP and PS.

2.3.4. Scanning electron microscopy

Micrographs on RB and PB, fractured at cryogenic temperature, were obtained from samples with and without superficial extraction of the PS dispersed phase. The extraction was done with THF at room temperature. From non-extracted samples the increment in particle-matrix adhesion as well as the decrement in particle size were

Table 1
Designation and description of all samples prepared

Sample	Description	Catalyst content (wt%)
PPp	Processed PP	0
PSp	Processed PS	0
PB	Physical blend	0
RB01	Reactive blend	0.1
RB03	Reactive blend	0.3
RB05	Reactive blend	0.5
RB07	Reactive blend	0.7
RB10	Reactive blend	1.0
RPP	Pure PP upon FC reaction	0.1–1.0
RPS	Pure PS upon FC reaction	0.1–1.0

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[1] All percentages are expressed as wt% in the present work.

observed. The particle sizes were measured from the extracted samples. As the continuous phase (PP) retains the shape, at these extraction conditions, the remaining holes provide a direct measure of PS particle size. The electron microscope used was a JEOL JSM-35 CF with secondary electron detector. The samples were coated with Au in a sputter coater PELCO 91000. Analysis PRO™ software was used for processing the particle size data. About 300 particles where considered to calculate these parameters. The average diameters with its dispersion (standard errors) were plotted vs. catalyst concentration in order to build the emulsification curve.

Table 2
Average molecular weight and polydispersity of the homopolymers and the 'processed' ones

Sample	M_w (g/gmol)	M_w/M_n
PP	303,000	4.4
PPp	300,000	4.4
PS	278,000	2.2
PSp	275,000	2.3

3. Results and discussion

3.1. Chemical aspects

In this work, FC reactions were carried out on PP/PS blends to obtain compatibilizing graft copolymers PP-*g*-PS. Their general mechanism is expected to be similar to the most common one suggested for PE-*g*-PS formation in the literature [12–14]. It is important to consider that both PP and PS are susceptible to suffer chain scission (β-cleavage) due to the presence of tertiary and benzyl carbon atoms, respectively [15,16]. Consequently, certain amounts of low-M_w PP and PS can be expected as by-products. This is a general scheme for the PP-*g*-PS formation:

In order to ascertain the possible occurrence of chain scission and/or crosslinking side reactions, a systematic study was performed. The possibility of thermal degradation was analyzed for both pure polymers and physical blends. The processing routine explained in Section 2 was applied to the raw materials, and the products were characterized. The SEC curves of 'processed' homopolymers, namely PPp and PSp, closely matched those corresponding to the raw materials, thus indicating that they do not change with the processing. This is confirmed by the average molecular-weight values (expressed as M_w) listed in Table 2. The FTIR results also agree. The homopolymers spectra before and after processing remain unchanged and the typical oxidation peak ($\approx 1700\ \mathrm{cm}^{-1}$) does not appear. The absence of oxidation was also verified for both PB and RB.

After checking that no thermal degradation was present, the homopolymers were reacted at the same conditions employed for RB. Then, the reaction products (RPP and RPS) were compared with the pure polymers (PP and PS). Table 3 shows the molecular weights and their polydispersities (M_w/M_n) for the initial and reacted materials. It is apparent that reacted polymers exhibit average molecular weights that are considerably lower than those of the unreacted ones, specially for $AlCl_3$ concentrations higher than 0.7%. These results clearly indicate that chain scission is produced by the FC reaction at high catalyst contents, but no evidence of crosslinking was detected in the high molecular weight region of the SEC chromatogram.

Table 3
Average molecular weight and polydispersity for reacted homopolymers (RPP and RPS)

Percentage of $AlCl_3$	RPP M_w (g/gmol)	RPP M_w/M_n	RPS M_w (g/gmol)	RPS M_w/M_n
0.1	303,000	4.4	275,000	2.2
0.3	298,000	4.3	260,000	4.2
0.5	240,000	4	228,000	5.3
0.7	165,000	3.5	<20,000[a]	–
1.0	56,000	2.7	<20,000[a]	–

[a] Out of detection range of the SEC columns employed.

3.2. Morphological aspects

The emulsification effect of an interphase modifier in immiscible polymer blends, is directly related to the interfacial tension reduction caused by such modifier. Since the interfacial tension is proportional to the particle size of the dispersed phase [17–19], the emulsification behavior can be assessed from particle size variation with the concentration of copolymer formed. Several authors have reported that the emulsification effect (related to compatibilization efficiency) reaches a maximum when the interphase is saturated with the modifier. At this point, the interfacial tension and particle size are minimum and the critical micelle condition (cmc) is reached [3,8]. Above cmc the interfacial tension as well as the particle size remain constant. Any copolymer in excess to cmc will form micelles, which will stay within the homopolymer phases, not contributing to the emulsification process.

In our previous work [10], the cmc for the present system was assessed. The cmc condition was reached at 0.7% of catalyst. The particle size shows an exponential decay, revealing the reaction progress. As it is shown in Table 4, a significant drop in particle size with the first amount of catalyst added is observed. From RB07, particle diameter remains constant and cmc condition is reached. Since all the samples were processed at the same mixing conditions, any decrease in particle size can be attributed to interphase modifications produced by the PP-*g*-PS, formed during the FC reaction. Taking into account that the particle size

Table 4
Disperse-phase average diameter (D_p) and standard deviation ($\sigma(D_p)$) for physical and reactive blends

Blend	D_p (μm)	$\sigma(D_p)$ (μm)
PB	1.42	0.3
RB01	0.91	0.2
RB03	0.81	0.14
RB05	0.62	0.1
RB07	0.47	0.07
RB10	0.46	0.05

decreases to one third of its initial value, reaching an equilibrium diameter of about 0.5 μm, the copolymer formed by the FC reaction can be considered as an efficient in situ compatibilizer for the PP/PS blend.

The emulsification data closely correlates with the observed adhesion between phases. Fig. 1 shows micrographs of the fracture surfaces corresponding to PB, RB03, RB07 and RB1. As the copolymer content increases, a consistent improvement in adhesion is clearly observed along with particle size decreasing. It also appears that for catalyst concentration equal or higher than 0.7% the interphase becomes almost undiscernibly, indicating a very good adhesion.

3.3. Mechanical properties

The mechanical behavior of a blend is determined by the contribution of each component, as well as by the blend morphology and the interfacial adhesion. Elongation at break and toughness, which are sensitive to the load transfer between phases, are appropriate tools to monitor the adhesion between phases. On the other hand, tensile strength is related to morphology, domain size, and size homogeneity. For the same homopolymers in the blends, it can be expected that the smaller the particle size and standard deviation are, the higher the tensile strength becomes [20,21].

Fig. 2 shows the elongation at break and the tensile strength as functions of the amount of catalyst used. The elongation at break shows a slight increment (30% higher than the PB's value) up to 0.3% of catalyst. However, with 0.5% $AlCl_3$ the elongation at break is three times higher than the PB's. The maximum, which amounts to five times the reference value, is reached for 0.7%. Afterwards, at 1.0% the elongation at break drops steeply. The sharp increase in elongation at break is in agreement with the adhesion improvement showed in the micrographs (Fig. 1). Nevertheless, the significant decrease observed in this

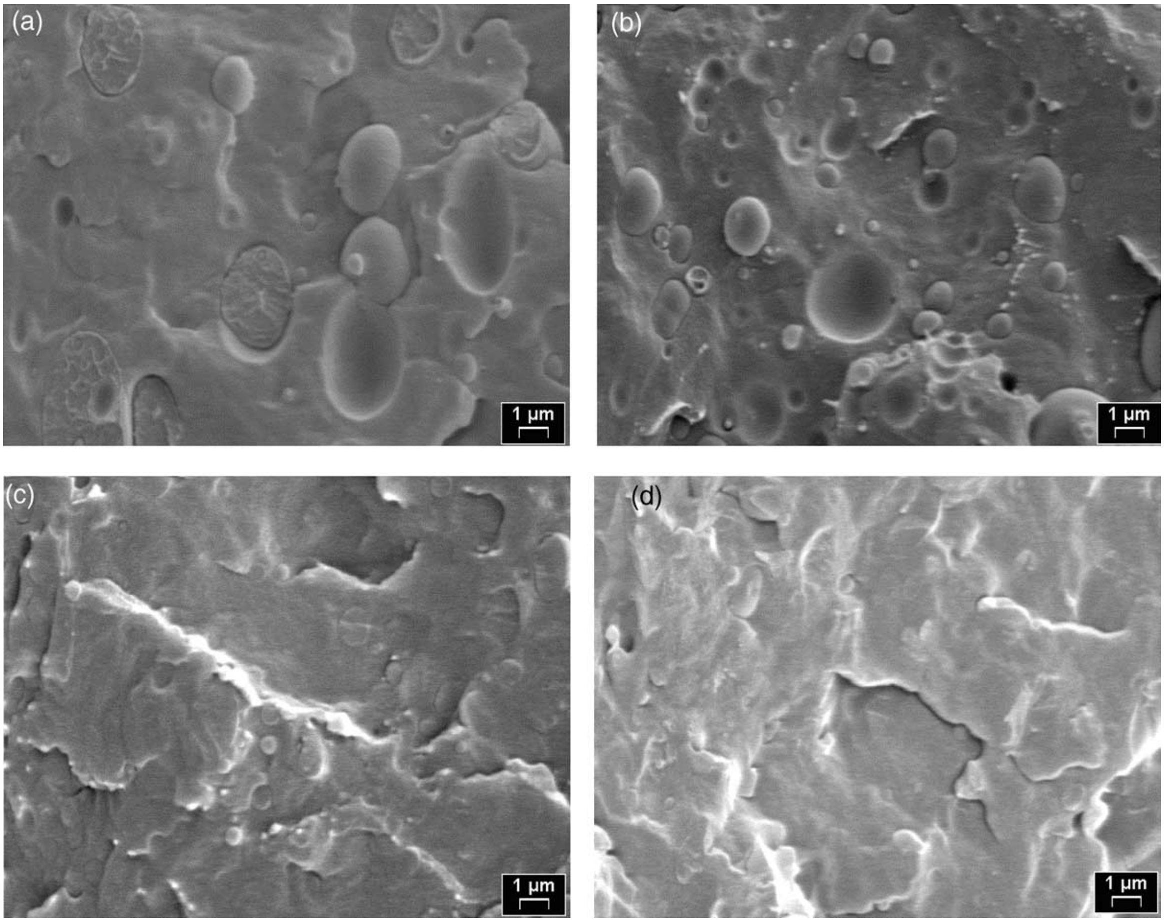

Fig. 1. SEM micrographs from (a) PB, (b) RB03, (c) RB07 and (d) RB1.

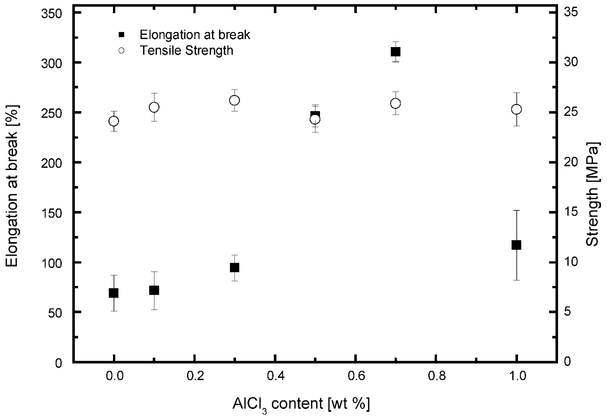

Fig. 2. Variation of elongation at break and tensile strength with de catalyst concentration for all blends prepared (Tensile Test).

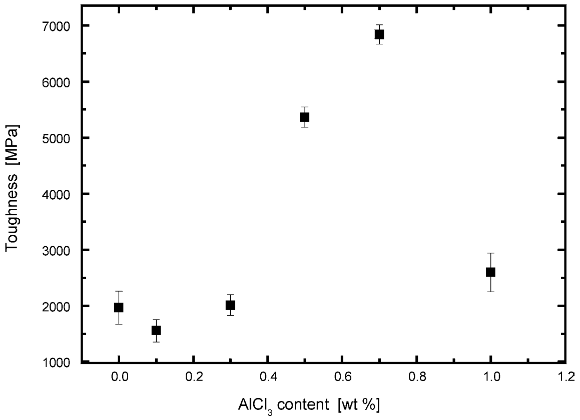

Fig. 3. Variation of toughness with the catalyst concentration under tensile test for all blends prepared.

property above 0.7% $AlCl_3$ seems to be contradictory since the corresponding micrograph (Fig. 1(d)) shows very good adhesion, which indicates a large elongation at break. On the other hand, the tensile strength behavior is different from the expected one. In spite of an average particle-diameter decay of one third for 1.0% catalyst (Table 4), the property remained essentially constant. In this case, in view of the smaller particle diameters, an increment in tensile strength would have been predicted.

These results are to be explained by taking into account that both PS and PP can suffer chain scission. With 0.7% catalyst, the M_n of the continuous phase (PP) decays only in 20%, whereas for 1.0% it diminishes in 70% with respect to its original value. It is known that the mechanical properties of polymers depend on their molecular weights. The higher the molecular weight, the higher both the tensile strength and elongation at break [20,21]. The RB1 blend contains a compatibilized interphase, and this feature improves the interfacial adhesion and decreases the particle size (Fig. 1(d)). On the other hand, the homopolymers in the RB1 have been modified by chain scission. These two effects contribute inversely to the mechanical properties. For catalyst contents higher than 0.7%, the chain-scission effect is large enough to reduce the elongation at break. The toughness variation with catalyst concentration, which is showed in Fig. 3, can be interpreted in terms of the previous explanation. It is clear that better-compatibilized blends are tougher, but when the polymer chain-length decreases (e.g. by chain scission), the toughness also tends to fall.

4. Conclusions

The simple-to-process low-cost Friedel–Crafts alkylation reaction was used for in situ compatibilization of PP/PS blends. This reaction forms a graft copolymer at the interphase, which behaves as a compatibilizer. It was found that there is a notorious emulsifying effect due to this interphase modifier. A net particle-size decrease along with catalyst content was obtained. Great improvements in both elongation at break and toughness were achieved. This result is in agreement with the interfacial adhesion observed in the morphological analysis. These properties increase with catalyst content up to maximum values, which are reached at 0.7%.

Side reactions that produce PP and PS chain scission occur for high catalyst contents. The corresponding molecular weight decrement was also considered for the interpretation of the mechanical behavior. For 1.0% $AlCl_3$, elongation at break and toughness dropped due to this effect, even when the interfacial adhesion was very good. The homopolymer chain scission also affected the tensile strength. This property remained invariable notwithstanding the particle size decay. Then, it can be inferred that the corresponding reduction in molecular weight must be compensating the strength increment.

The graft copolymer formed from the Friedel–Crafts reaction performs as a good compatibilizer for PP/PS blends at low catalyst concentrations. Considerable improvements in ductility and toughness were achieved without appreciable detriment to tensile strength even in the presence of chain scission reactions, provided the M_n PP reduction did not exceed 20%.

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